Structural Dependence of Bulk Modulus of Inorganic Glasses (Commemoration Issue Dedicated to Professor Megumi Tashiro on the Occation of his Retirement)

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An attempt to establish some basis for structural interpretation of elastic property of inorganic glasses from the theoretical and empirical relationships between bulk modulus and mean atomic volume of crystalline and glassy materials was reviewed. The relationships were derived on the assumption that the internal energy of a glass changes with the following three causes; (1) the change in Coulombic attraction force due to the ionic size difference of modifying cations or anions being substituted, (2) the change in packing state or coordination number of network forming cations, and (3) the change in excess volume of glassy state. The applicability of the simple atomic theory of elasticity based on Born potential was tested for various oxides and glasses. The inverse four-thirds power dependence of bulk modulus on volume, derivable theoretically for ionic crystals, was found to describe the effect of the first cause for alkali and alkaline earth silicate glasses. The effect of the second cause was examined for the data of polymorphs of SiO_2, GeO_2 and C, and the inverse fourth power or higher order relationship was established empirically. The result was applied to interpret the data of alkali germanate and lead borate glasses. The effect of the third cause was discussed by taking the densification of fused silica and the crystallization of lithium silicate glasses as examples.

KEY WORDS: Elastic properites/ Glass Structure/ Equation of state/

I. INTRODUCTION

The short range ordering of atoms in a glass is generally considered to be similar to that in the crystal having the same chemical composition, and many properties of glass can be analyzed as though the glass were a single crystal. Thus, knowledge of the structural dependence of physical properties of crystalline compounds is useful to discuss the glass structure from the experimental data of physical properites of glasses, although this approach is indirect compared with the small angle X-ray or neutron diffraction technique.

Among various physical properties, elastic properties are of particular interest, because they are directly related to the interatomic forces between nearest atoms in solids. In order to deduce the structural dependence of elastic properties of solids, each atom is generally assumed to be a point mass connected each other by spring having appropriate attractive and repulsive forces. This simple atomic theory of elasticity was introduced first by Born[1] to obtain the lattice energy and chemical potential of ionic crystals from compressibility data, and was applied, with some modifications, by Blackmann and others to interpret the compositional variation and structural dependence of elastic properties of various crystal compounds.[2,3] However,

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it is still quite difficult to calculate the elastic constants of oxides and silicates theoretically, because the chemical potentials between different atoms are not known even though their structures, or the locations of all atoms, are fixed. Thus, some empirical relationships have to be established even for crystalline solids.

In the past years, the present author and his co-workers have been trying to accumulate systematic data of elastic constants for different types of crystals and glasses, with a hope that some basis for structural interpretation of elastic constants of glasses could be established from the data of crystals and some insight into glass structure could be obtained from the elastic constants data of glasses. The present paper describes some of the results obtained so far and shows how one may utilize these experimental data in order to discuss the structure of glass.

II. APPLICABILITY OF SIMPLE ATOMIC THEORY

In order to obtain the structural dependence of elastic constants for glass forming oxides, it is important to know whether the classical theories established for ionic solids are applicable also for these oxides or not. According to the atomic theory of elasticity, the relationship between bulk modulus and volume for a solid can be obtained once the internal energy U is expressed as a function of interatomic distance r. Among various expressions of U, the simplest form applicable for ionic solids is the following Born potential consisting of the Coulomb's attractive and some repulsive forces,[1]

$$U=-\frac{AZ_1Z_2e^2}{r}+\frac{B}{r^n}, \tag{1}$$

where A is the Madelung constant, Z_1 and Z_2 are the effective charges of cations and anions, and B and n are parameters representing the contribution of the repulsive force. For alkali halides, n is from 9 to 12.[2] The internal pressure P is given by $-(\partial U/\partial V)_T$, and the bulk modulus K by $-V(\partial P/\partial V)_T$. Further differentiation of K with respect to P yields the following equation,[4]

$$K'=\left(\frac{\partial K}{\partial P}\right)_T=\frac{1}{3}(n+3)+\frac{4}{3}(n-1)\left[(n+3)\left(\frac{V}{V_0}\right)^{n-\frac{1}{3}}-4\right]^{-1}, \tag{2}$$

where V_0 is the volume at 1 atmosphere. If K' is taken at near 1 atmosphere, (V/V_0) is close to 1 and K' is approximated by $(n+7)/3$.

The values of K' reported in literature for oxides and silicates were compiled and listed in Table I. Table I also lists the values of n estimated for these compounds by Eq. (2). It is clear that they are within the range of $5\sim12$, close to those of alkali halides.[2] This result indicates that the internal energy of oxides may be represented, at least mathematically, by assuming the purely ionic Born potential. Although this is certainly against such a common knowledge of the bonding nature of oxides that a certain degree of covalency exists,[7] this assumption is useful as a tool not only to establish the compositional dependence of elastic property of oxide glasses but also to judge whether a glass behaves in a normal manner or not.

Since the value of n for the Born potential is from 5 to 12 for a regular solid as

Table I. Pressure Derivative of Bulk Modulus and Repulsive Parameter n for Oxides and Silicates (Ref. 4~6)

	K'	n		K'	n
BeO	5.5	9.5	Fe_2O_3	4.5	6.5
MgO	4.5	6.5	Mg_2SiO_4	4.5	6.5
CaO	5.2	8.7	$MgAl_2O_4$	4.2	5.6
ZnO	4.8	7.4	α–SiO_2	6.4	12.2
Al_2O_3	4.0	5.0	Garnet	5.4	9.3

Table II. Pressure Derivative of Bulk Modulus for Various Glasses

Glass Composition	K'	Ref.
(Mg, Ca, Sr, Ba) SiO_3	5.5~6.2	8
Calcium Aluminate	4.0~4.7	9
$3Na_2O{\cdot}2TiO_2{\cdot}5SiO_2$	4.8	10
$Na_2O{\cdot}1.5SiO_2$	5.7	11
$Na_2O{\cdot}2SiO_2$	4.6	11
$Na_2O{\cdot}4SiO_2$	1.6	11
SiO_2	−6.2	12
$Na_2O{\cdot}(2\sim10)\ B_2O_3$	4.6~6.1	13
B_2O_3	5.53	13
GeO_2	0.7	14

described above, a glass should have the value of K' from 4 to 6, if the glass behaves as though it were a single crystal. Table II lists the data for various glasses. Although some of the glasses with high SiO_2 contents have negative values of K' as pointed out first by Bridgman,[15] the values of K' for $RSiO_3$ glasses (R: mixture of Mg, Ca, Sr, and Ba) fall between those of α-quartz and MgO or CaO. Alkali silicate glasses with a large amount of alkali contents also have the values of K' between 4 and 6. Thus, the equations derived from Eq. (1) can be applied on both crystalline and glassy states of oxides and silicates in order to discuss the compositional variation of elastic properties of glass. Among various elastic constants and moduli, the bulk modulus is treated here mainly because it can be obtained directly from Eq. (1).

III. COMPOSITIONAL VARIATION IN ELASTIC CONSTANTS OF GLASS

1. Substitution of Ions in Glass.

When the Born potential of Eq. (1) is assumed, the bulk modulus K may be expressed as a function of volume as follows,[2]

$$K=\frac{1}{9}A{\cdot}Z_1Z_2e^2(n-1)C{\cdot}V^{-4/3}, \tag{3}$$

where C is a constant related to the packing condition of atoms or ions in the solid. If one takes a series of compounds such as alkali halides, the parameters A, n and C

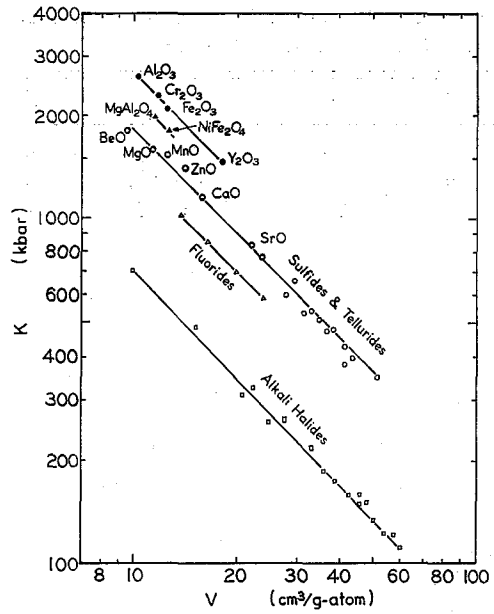

Fig. 1. Bulk Modulus-Volume Relationship for Various Crystalline Solids. (Refs. 6, 16)

in Eq. (3) are considered to be constant. Thus, it is expected that their bulk moduli vary in reciprocal proportion to the four-thirds power of the volume. This relation for a series of crystalline compounds is shown in Fig. 1.

As for glasses, the density of a glass is generally lower than that of the crystal having the same composition. Thus, the packing condition of ions in a glass is different from that of the crystalline state. However, the X-ray or neutron diffraction studies by various workers have shown that the coordination number of cations and the average interatomic distance between two neighbouring atoms in a glass are not so much different from those in the comparable crystal. Thus, the total volume of a glass may be assumed to be expressed as follows,[17]

$$V_G = V_C + \Delta V_G , \tag{4}$$

where ΔV_G is the excess volume of glassy state arising from the lack of long-range order in the glass sturcture. If the network structure is not affected by the addition or substitution of ions from one kind to another, the value of ΔV_G remains the same, and thus the change in glass volume results mainly from the addition or substitution of ions similar to that observed in a series of crystalline compounds. In this situation, the internal energy and bulk modulus should change in accordance with Eqs. (1) and (3), respectively. This approach was tested for various alkali and alkaline-earth silicate glasses,[17,18] and the results were shown in Figs. 2 and 3. Although there exists some scatter, the data points lie near the line having the slope of $-4/3$ as expected from Eq. (3). In other words, the variation of K for these glasses results mainly from the change in volume caused by the difference in cationic size of modifying ions.

A similar discussion can be made for the case that GeO_2 glass and GeS_2 glass are

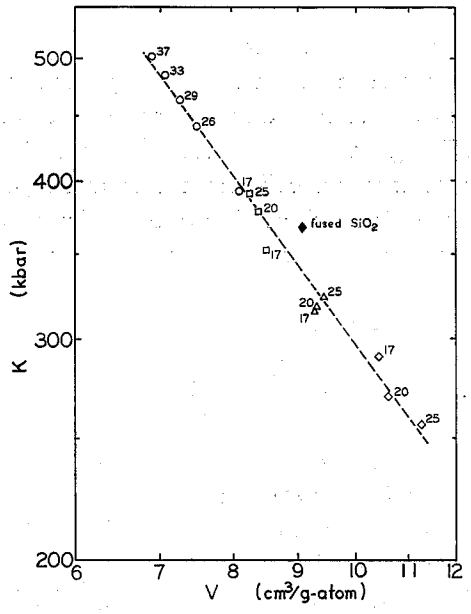

Fig. 2. Bulk Modulus-Volume Relationship for Alkali Silicate Glasses. The slope of line is $-4/3$, and the numbers by the points represent alkali oxide contents in mol%. (○) Li, (□) Na, (△) K, (◇) Cs. (Ref. 18)

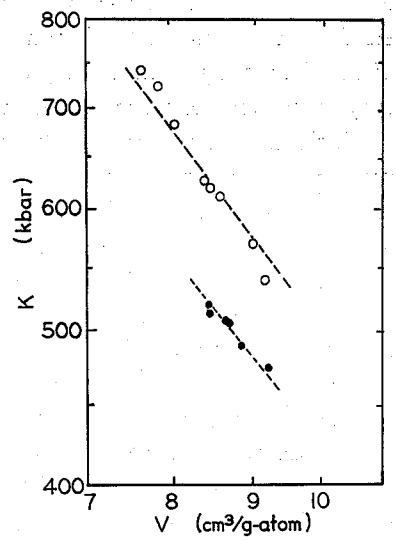

Fig. 3. Bulk Modulus-Volume Relationship for Alkaline Earth Silicate Glasses. The Slope of lines is $-4/3$. (○) $RSiO_3$ composition, (●) RSi_2O_5 composition, where R is Mg, Ca, Sr, Ba or their mixture. (Ref. 17)

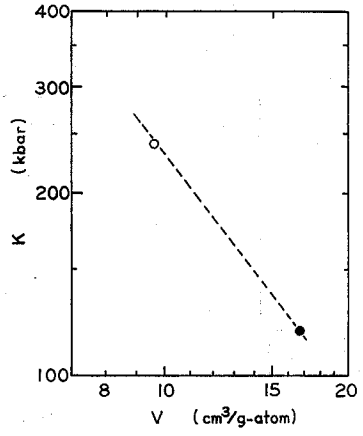

Fig. 4. Bulk Modulus-Volume Relationship for GeO_2 and GeS_2 Glasses. The slope of line is $-4/3$. (○) GeO_2, (●) GeS_2. Data are from Refs. 14 and 19.

compared. As shown in Fig. 4, the slope is close to $-4/3$, so that the variation in K for these glasses can be explained by the difference in anionic size between oxygen and sulfur.

2. Change in Packing Condition in Glass.

From the assumption made to derive Eq. (3), it is clear that Eq. (3) is not applicable as it is, when cations are substituted by those belonging to a different group in the periodic table, because the bonding nature as well as the packing condition becomes different and the parameters A, n and C in Eq. (3) may change considerably. Since many of network forming oxides are known to take two different coordination states with little change in cation-anion distance, the effect of the change in packing condition or coordination number on the internal energy is important to clarify the compositional variation of elastic constants of glasses. However, the nature of the binding energy between network forming cations and oxygen ions is not well known and thus it is not possible at this moment to derive an appropriate bulk modulus-volume relationship theoretically. An empirical approach has to be employed based on the data of polymorphs of crystalline compounds.

The bulk modulus-volume relationship for various polymorphs of SiO_2 and GeO_2 are shown in Fig. 5. It is clear that K varies with inverse fourth power of V when the coordination number changes from four to six for both SiO_2 and GeO_2, while the substitution between Si and Ge in the same crystal structure follows the inverse four-thirds power relationship described in the previous section. In this figure, the data

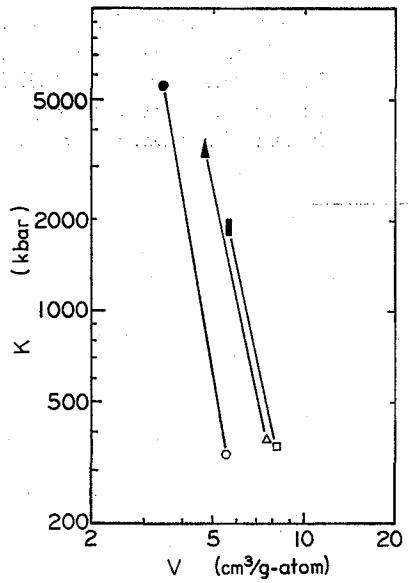

Fig. 5. Effect of Change in Coordination Number of Cations on Bulk Modulus. (○) graphite, C is surrounded by 3C, from Ref. 20; (●) diamond, C by 4C, from Ref. 20; (△) α-quartz, Si by 4O, from Ref. 21; (▲) stishovite, Si by 6O, from Ref. 22; (□) α-quartz type GeO_2, Ge by 4O, from Ref. 23; (■) rutile type GeO_2, Ge by 6O, from Ref. 23.

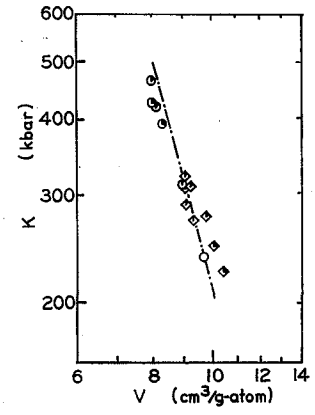

Fig. 6. Bulk Modulus-Volume Relationship for Na_2O–GeO_2 and Na_2S–GeO_2 glasses. (○) Na_2O–GeO_2, (□) Na_2S–GeO_2. The dark shading represents Na_2O or Na_2S content in mol%. The slope of line is the same as that for GeO_2 polymorphs in Fig. 5. (Ref. 24)

of diamond and graphite are also given in order to show that the change in network structure from the two-dimensional to the three-dimensional structure for a covalent solid gives the inverse sixth power relationship, slightly steeper than that for SiO_2 or GeO_2.

There are a number of glasses in which cations are believed to change their coordination states depending upon glass composition. Alkali germanate glass is such an example. From the above consideration, it is expected that they should follow the relationship observed for GeO_2 if such a coordination change takes place. The results of Na_2O–GeO_2 and Na_2S–GeO_2 glasses are given in Fig. 6, which shows that this expectation is satisfied. The shift of data for Na_2S–GeO_2 glasses from the line may be due to the substitution of oxygen by sulphur described in the previous section. On the other hand, the results of Na_2O–SiO_2 given in Fig. 2 follows the inverse four-thirds power relationship as expected from the Born potential, indicating no change in coordination state of Si in these glasses.

Another example is lead borate glass. When PbO is added to B_2O_3 glass, the bulk modulus increases with PbO up to 44 mol% PbO and then decreases with PbO. As shown in Fig. 7, the change in bulk modulus with volume for the glasses with PbO contents is fast, while that for the glasses with high PbO contents is slow. In the same figure, the data of lead silicate glasses are shown for the sake of comparison. Although there exists some scatter, the bulk modulus decreases with increasing PbO

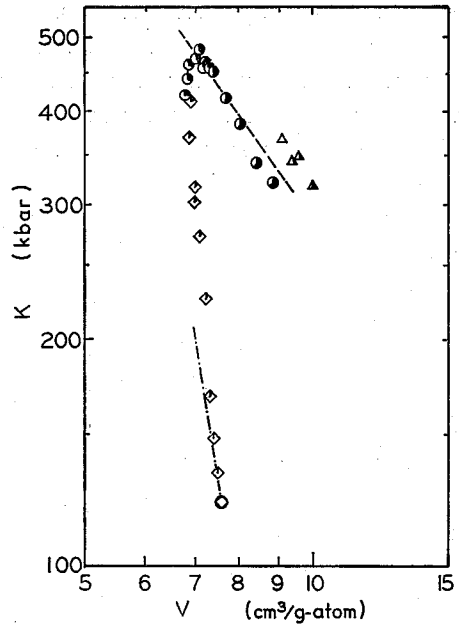

Fig. 7. Bulk Modulus-Volume Relationship for PbO–B_2O_3 and PbO–SiO_2 Glasses. (◇) PbO–B_2O_3 immiscible glasses, from Ref. 25, (○) PbO–B_2O_3 miscible glasses, from Ref. 26, (△) PbO–SiO_2 glasses from Ref. 25 and 27. The dark shading represents PbO content in mol%. The slope of broken line is −4/3, and that of chained line is the same as that for C polymorphs in Fig. 5.

up to 70 mol%PbO without any apparent sudden change from 0 to 70 mol%. These results seem to indicate that the state of boron ions changes from BO_3 to BO_4 with addition of PbO. This is in accordance with the results of NMR measurements on lead borate glasses by Bray,[28,29] who showed that BO_3 units change into BO_4 units with increasing PbO up to 50 mol% but goes back to BO_3 units above 50 mol% PbO. The reason why this disappearance of BO_4 units does not appear in the bulk modulus-volume relation may be attributed to the fact that the amount of PbO_4 units in glass becomes high and the change in the state of boron ions from BO_4 to BO_3 does not disturb the packing state of atoms so much.

3. The Excess Volume of Glassy State.

The above treatment is based on an assumption that the excess volume of the glassy state ΔV_G shown in Eq. (4) remains unchanged in spite of compositional variation. This assumption may be satisfactory for a limited range of glass compositions, but when glasses of a wide compositional range are to be treated, this assumption may not hold and the variation in ΔV_G due to the substitution of constituent ions in glass or the change in packing condition has to be taken into consideration. In such case, the elastic constants of two glasses should be different depending upon the magnitude of ΔV_G. Such effect of ΔV_G may be similar to the effect of porosity in polycrystalline materials on elastic constants. Their elastic constants are affected not only by the amount of porosity but also by the shape of pores, even if the pores are distributed uniformly. When pores of narrow shape exist, the change in bulk modulus with volume becomes extremely large. Thus, it is not possible at the present moment to deal with this effect quantitatively, and in the present author's opinion, this is the reason why the elastic constants of glasses can not be expressed as a linear function of constituent oxides. However, it seems possible to judge qualitatively whether some structural change takes place or not.

In Fig. 8, the bulk modulus-volume relationship for densified fused silica is shown. The densified samples were made by applying 45–80 kbars isostatic pressures at 500–600°C, and had the density ranging from 2.35–2.60 compared with 2.203 for fused silica.[30] It is clear from Fig. 8 that the densified fused silica follows the inverse four-thirds power relationship at the beginning. This seems to indicate that the average interatomic distance is being changed with little change in glass structure at the low pressure range. However, as pressure is increased and glass is densified more, the bulk modulus increases sharply with volume by following the inverse fourth power relationship which indicates the occurance of change in glass structure. The closeness of the bulk modulus of a densified glass to that of β-quartz may be coincident, but might suggest that the average angle of Si–O–Si is similar to that of β-quartz or 180°. When more pressure is applied, the bulk modulus starts to increase rapidly again, indicating another structural change.

A sudden change in the bulk modulus-volume relationship can be seen when the transition from the glassy state to the crystalline state takes place, as examplified for $Li_2O{\cdot}2SiO_2$ or $Li_2O{\cdot}4SiO_2$ glasses shown in Fig. 9. Obviously, such a large change in bulk modulus is associated with the disappearance of ΔV_G in these glasses. However,

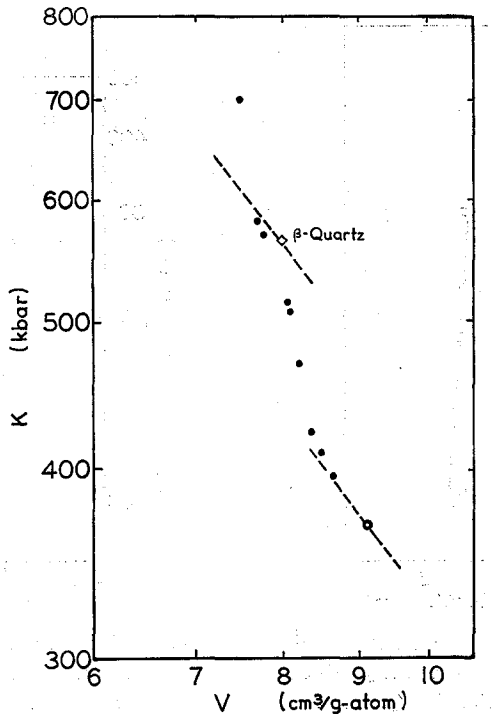

Fig. 8. Bulk Modulus-Volume Relationship for Densified Fused Silica. The slope of lines is $-4/3$. The open circle is for regular fused silica. (Ref. 30)

this behavior is different from the effect of crystallization for chalcogenide glass and glassy metals, which shows the inverse fourth power relationship similar to that for polymorphic transitions or polycrystalline materials with spherical pores (Figs. 10 & 11.) Thus it is considered that the crystallization of silicate glasses involves more complicated structural changes than that of glassy metals or chalcogenide glass.

When the bulk modulus-volume relationship for glasses deviates from that of the expectation described above, there should be a reason for such deviation. One example is the case of mixed alkali silicate glasses. The bulk modulus-volume relationship, shown in Fig. 12, indicates a positive deviation from the linear additivity of two end members. This deviation may be attributed to the tightening of network structure of mixed alkali silicate glasses or to the change in ΔV_a.

It should be emphasized here that the above consideration based on the bulk modulus-volume relationship is simple and may not be enough to give structural interpretation of elastic property for more complicated glasses. A major difficulty arises from the fact that glass is elastically isotropic and no unique solution exists to describe such an average property of elastic constants on the basis of atomic arrangement in glass sturcture. However, by combining with the information about the short range ordering of glass obtained by the small angle X-ray or neutron diffraction method, the present approach seems to provide additional information about glass structure.

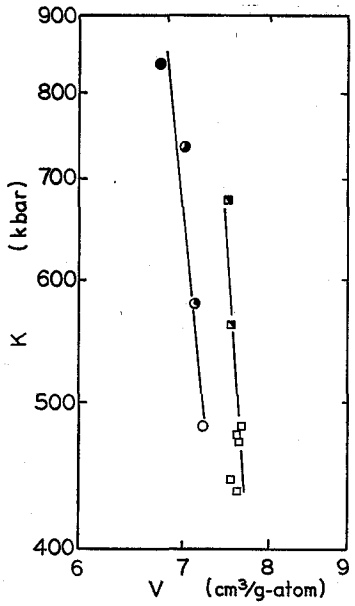

Fig. 9. Effect of Crystallization on Bulk Modulus for $Li_2O{\cdot}2SiO_2$ and $Li_2O{\cdot}4SiO_2$ Glasses. (○) $Li_2O{\cdot}2SiO_2$ glass and glass ceramics, estimated from Youngs modulus data in Ref. 31 and constant Poisson's ratio, (□) $Li_2O{\cdot}4SiO_2$ glass and glass ceramics calculated from the data in Ref. 32. The dark shading represents the volume fraction of crystals.

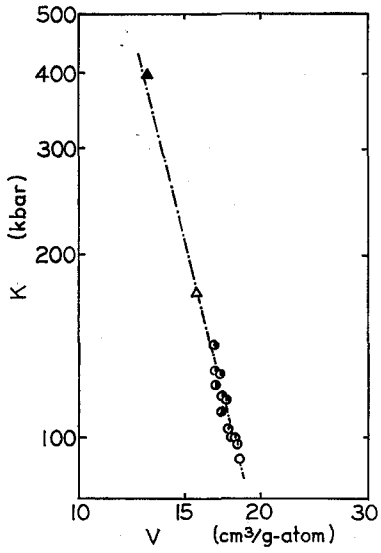

Fig. 10. Bulk Modulus-Volume Relationship for Various Glasses and Crystals made of Se and As. (△) As crystal, (▲) Se crystal, (○) As–Se glasses. The dark shading represents As content in mol%. The slope of line is −4. (Ref. 33, 34)

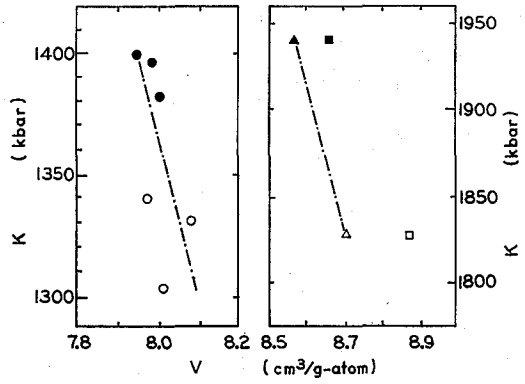

Fig. 11. Effect of Crystallization on Bulk Modulus for Glassy Metals. (○) Sm_2Co_{17}, from Ref. 35, (□) $Pd_{80}Si_{20}$, (△) $Pd_{78}Si_{16}Cu_6$, both from Ref. 36. Open circles are glassy state. The slope of lines is −4.

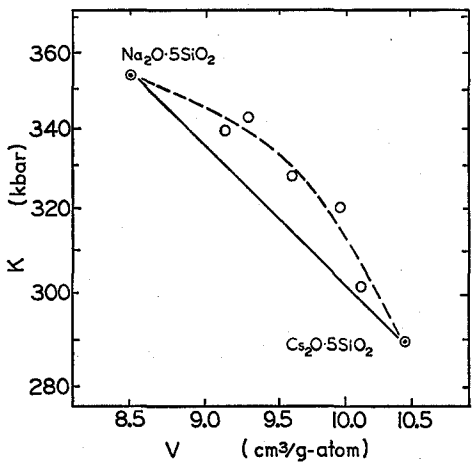

Fig. 12. Bulk Modulus-Volume Relationship for Mixed Alkali Glasses.

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